Fuel Processing:

Fuel and Fuel Constituents Effects on Fuel Processor and Catalyst Durability and Performance

Catalyst Designs for Improved Fuel Processing and Gas Clean-up within PEM Fuel Cell Engines

ESA-EPE Fuel Cell Team

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Fuel Processing Technical Objectives

Objectives

- Quantify fuel processor performance to identify effects of various constituents and contaminants in fuels.
- Measure fuel composition effects on performance of individual components in the fuel processor.
- Measure and quantify catalyst durability and fuel and fuel impurity effects on catalyst durability.
- Understand the parameters that affect fuel processor lifetime and durability.
- Measure effects of real reformate on the operation of clean-up devices such as the PrOx and on fuel cell stack performance.

Fuels for Fuel Cell Testing Approach

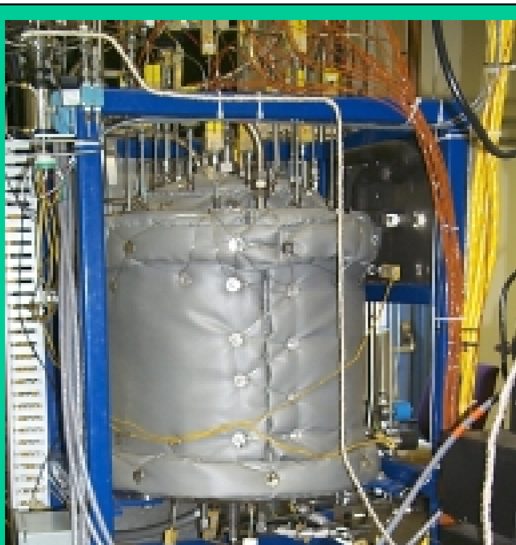
- Fuel Effects on Fuel Processing
  - Examine fuel components
  - Examine fuel impurities
  - Fuel effects on durability
    - Carbon formation
    - Catalyst degradation
  - Fuel effects on start-up

- Catalyst Testing
  - Isothermal reactor testing
  - Adiabatic reactor testing
    - Fuel components
    - Fuel impurities
    - Life-time / durability
    - Carbon formation

- Fuel Processor Testing
  - Fuel processor types
    - gas phase / catalytic
    - integrated / non-integrated
  - Efficiency/performance measurement
    - Mass / energy balances
    - Fuel processing effluent
  - Effects on system components

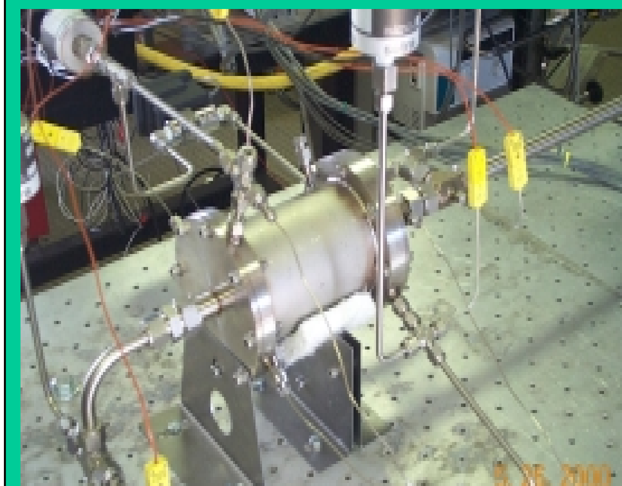
- Catalyst Characterization
  - Degradation / durability
    - Delineate degradation mechanisms
  - Catalyst activity measurement
    - Surface area/particle size

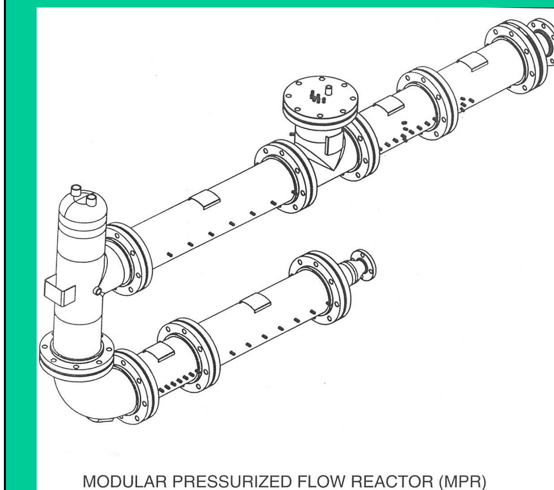
LANL Fuel / Catalyst Testing Facilities



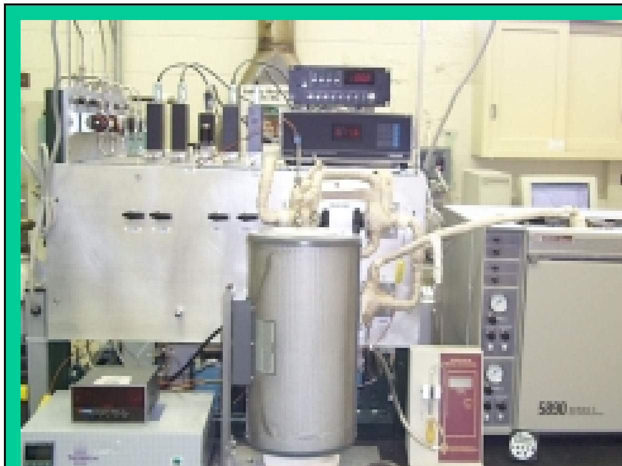
Thermally integrated fuel processor (HBT)

LANL Adiabatic Partial Oxidation/Steam Reforming





Modular dis-integrated fuel processor (Epyx)



Micro-scale Isothermal catalyst test-bed

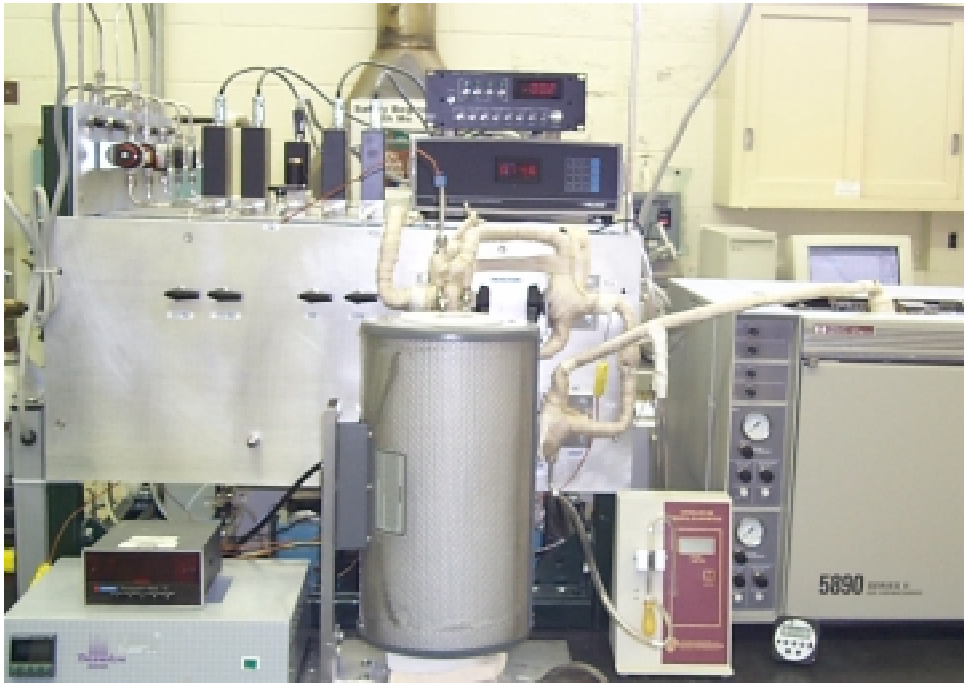
LANL Fuels For Fuel Cells Testing 2000 - 2001

- Fuel Testing
  - Gasoline individual components
    - aliphatic
    - aromatic
    - napthenic
    - unsaturated
  - Blends of individual components
  - Ca ref. gasoline
  - Natural gas
  - Methane
  - Impurities
    - Sulfur

- Integrated fuel processing system
  - HBT - 50 kWe
  - Fuel / system efficiency
- Microscale reactor (iso-thermal)
  - fuel components
  - catalysts
- LANL adiabatic catalytic
  - operational May
  - use for fuels effects
    - in situ carbon formation monitoring
- Modular reactor (Nuvera [EPYX])
  - operational July
- Compare fuel effects
  - catalytic reactions
  - gas phase reactions

Micro-scale Catalyst Test Facility

Isothermal Reactor for catalyst and process evaluation



- Gas analysis equipment:
  - Gas Chromatograph
  - Mass Spectrometer
  - GC-MS
- Catalyst characterization techniques available:
  - XRD
  - BET / Chemisorption
  - XRF
  - SEM / EDS
  - TEM

Low catalyst loading (< 500mg)

Isothermal Operation

Reactant Control

Contaminant Effect

Catalyst Lifetime

Carbon (Soot) Formation

$2CO \Leftrightarrow C + CO_2$ (Boudouard Reaction)

$CH_4 \Leftrightarrow C + 2H_2$ (CH_4 Decomposition)

$CH_4 \rightarrow C_2H_6 + H_2 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + H_2 \rightarrow$ aromatics $+ H_2 \rightarrow$ soot

$C_nH_{2n} \rightarrow C_n + nH_2$

Formation of heavier hydrocarbons such as polycyclic aromatic compounds from aromatics

Structural change of catalyst particle (sintering, ….)

Fuel impurities change catalyst activity (poison)

Methods to help delineate catalyst degradation:

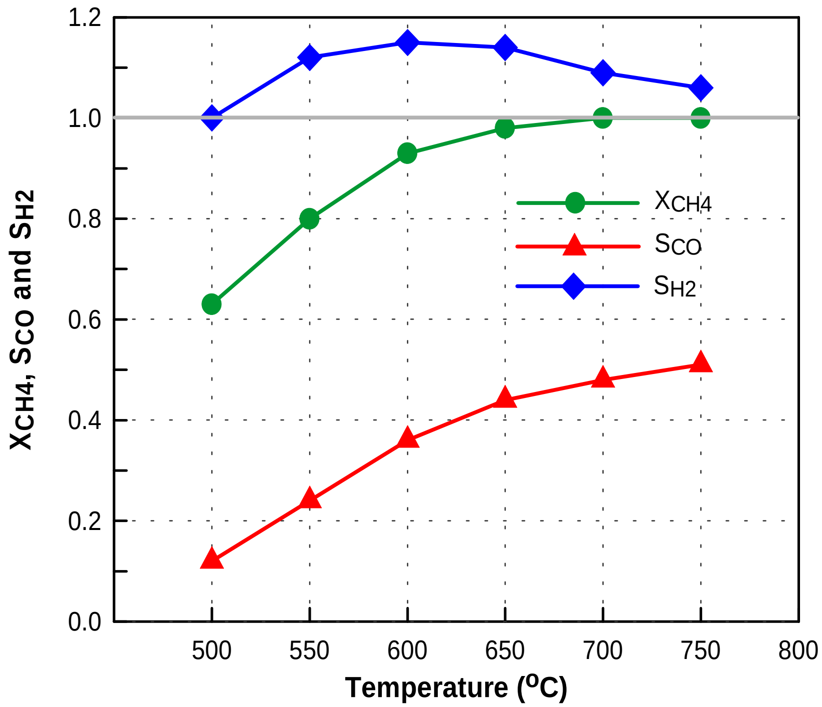
Monitor catalyst activity and performance

Measure carbon formation

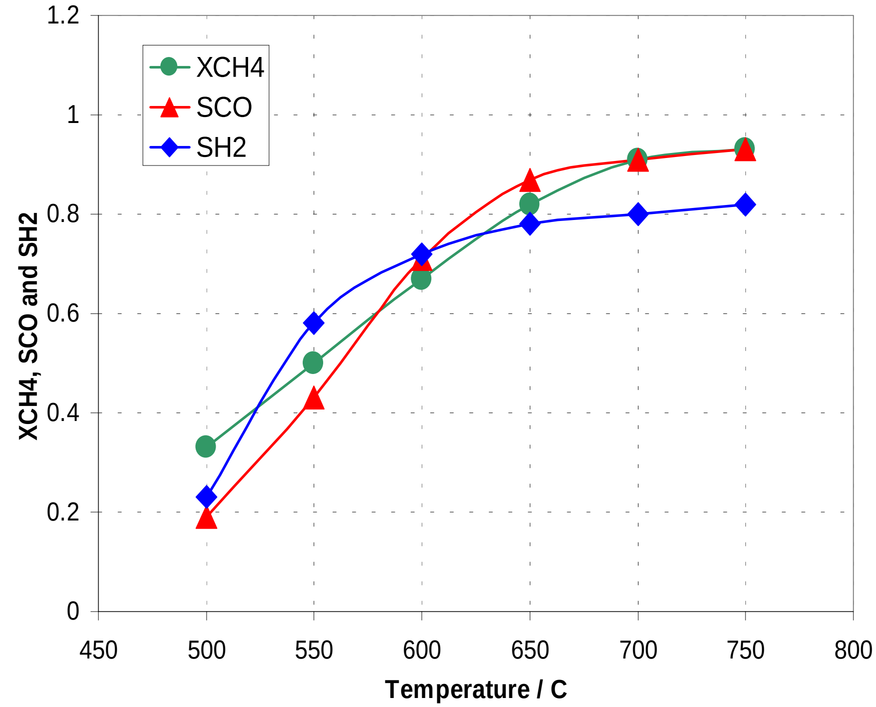
Analyze catalyst particles for changes in surface area, elemental composition

‘Isothermal’ POX of CH_4 with Temperature

Ni/Al_2O_3



Rh/Al_2O_3

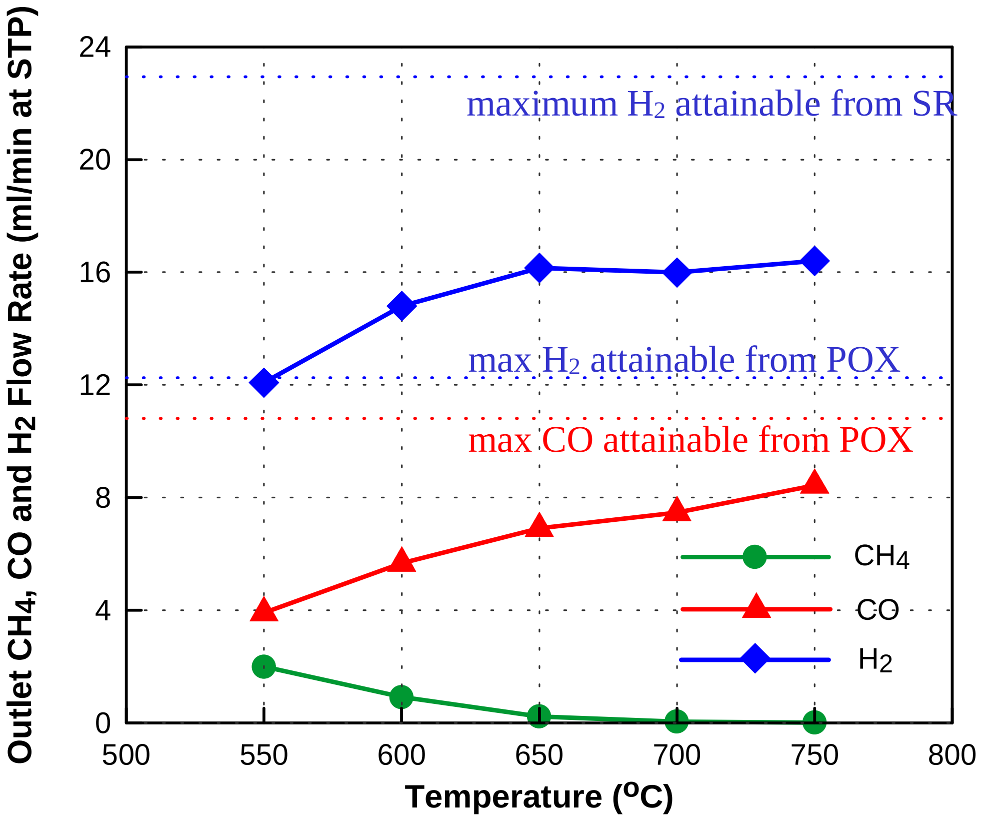


X_{CH4} = Methane Conversion

S_{CO} = CO,out/(CH_4,in - CH_4,out)

S_{H2} = 0.5xH_2,out/(CH_4,in - CH_4,out)

'Iso-thermal' POX-SR of iso-Octane



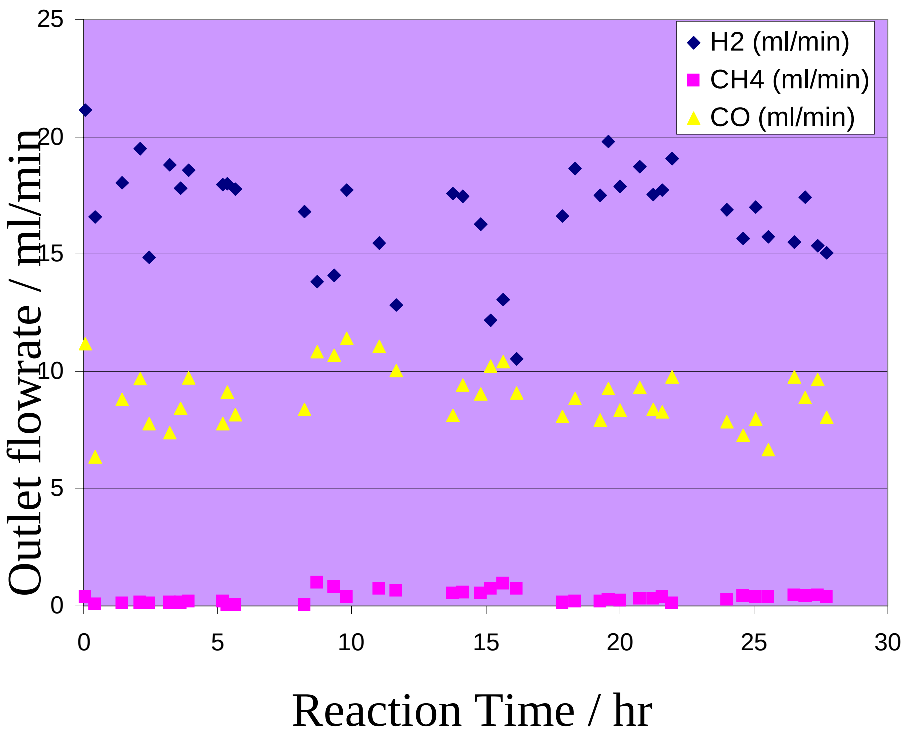
$C_8H_{18} + 4(O_2 + 3.76N_2) + 9H_2O + 10He$

Addition of H_2O promotes H_2 production via SR or WGS reaction

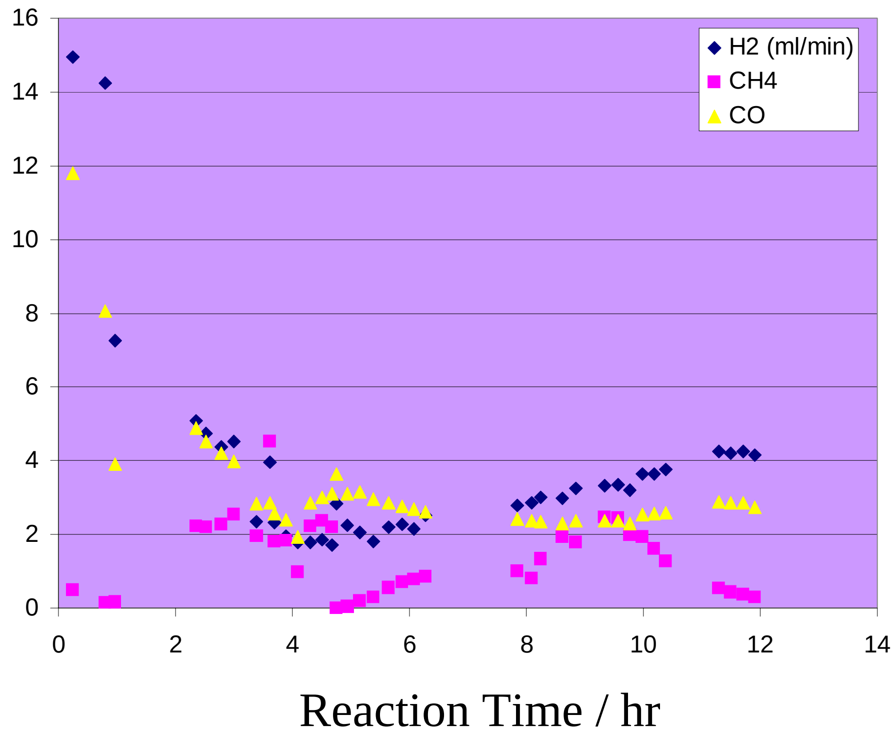
Partial oxidation of Iso-octane over Ni/Al_2O_3

(750^oC, O/C = 0.76, H_2O/C = 1.15)

iso-Octane



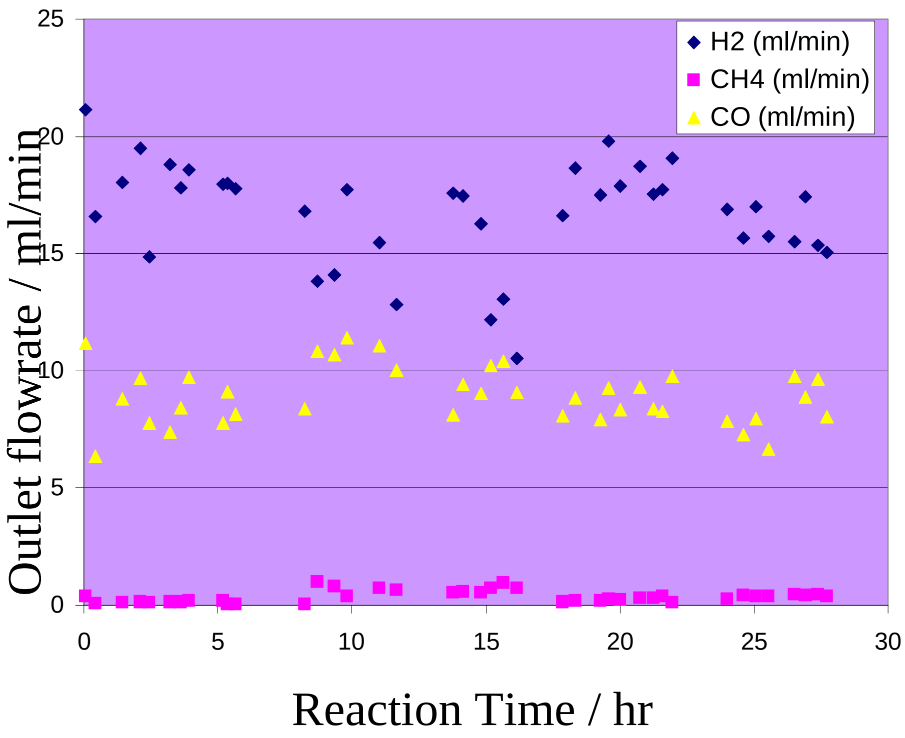
100 ppm Sulfur in iso-Octane



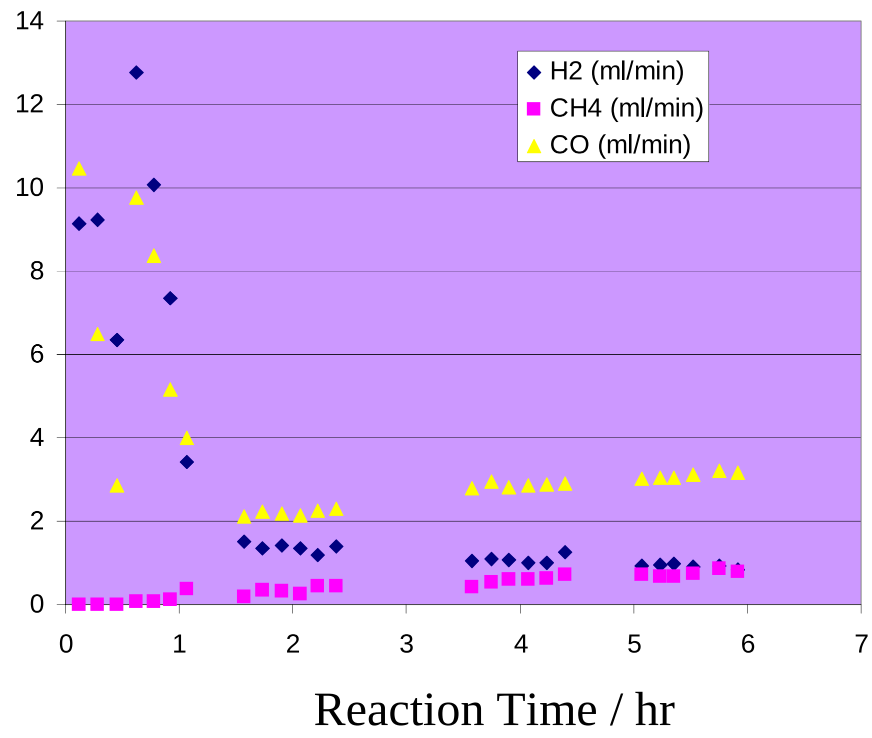
Partial oxidation of iso-Octane over Ni/Al_2O_3

(750^oC, O/C = 0.76, H_2O/C = 1.15)

iso-Octane



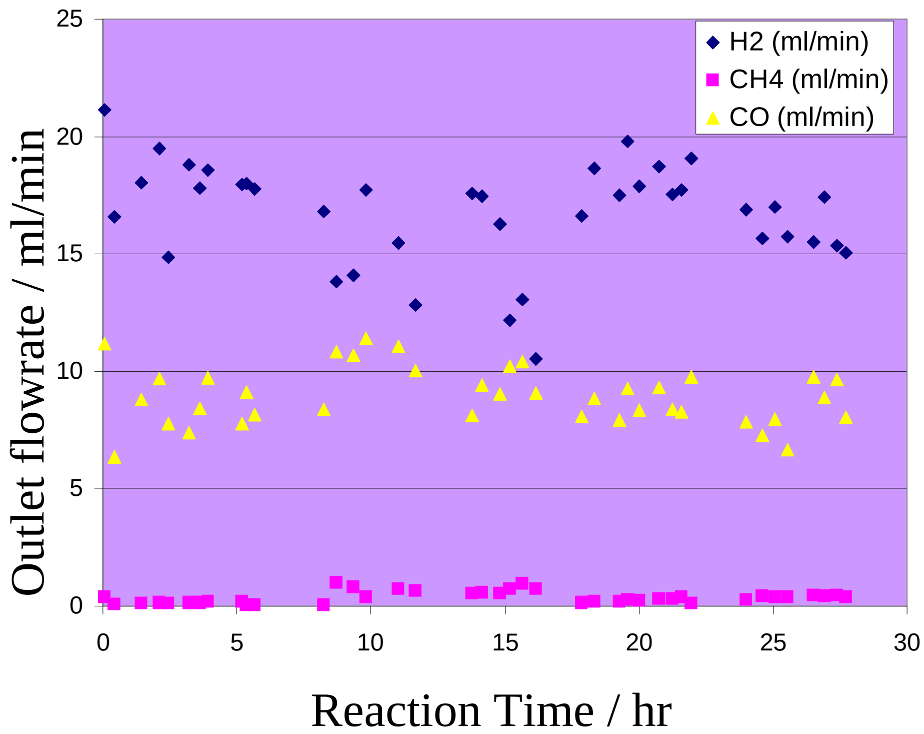
300 ppm Sulfur in iso-Octane



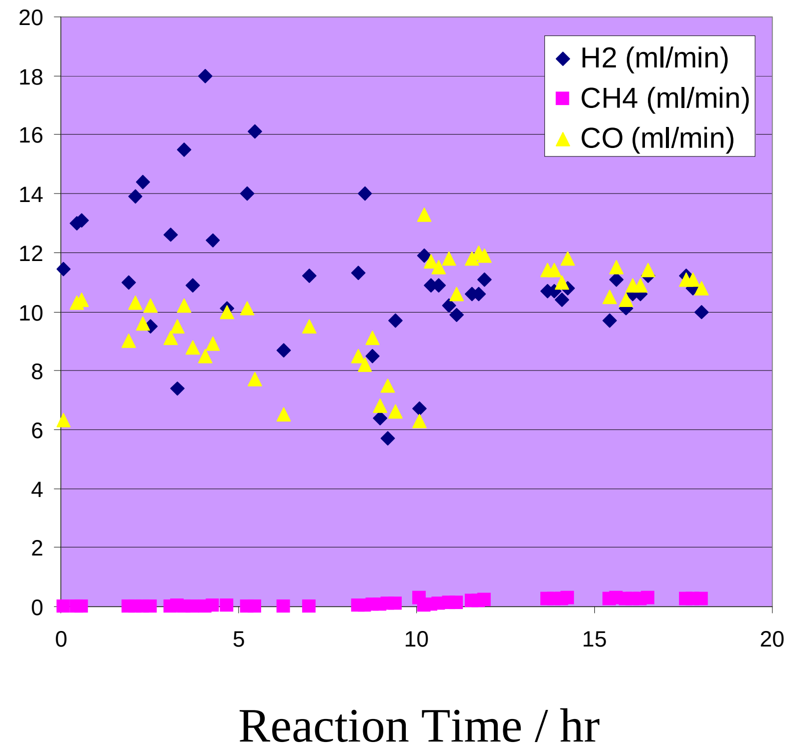
Partial oxidation of p-xylene over Ni/Al_2O_3

(750^oC, O/C = 0.76, H_2O/C = 1.15)

iso-Octane



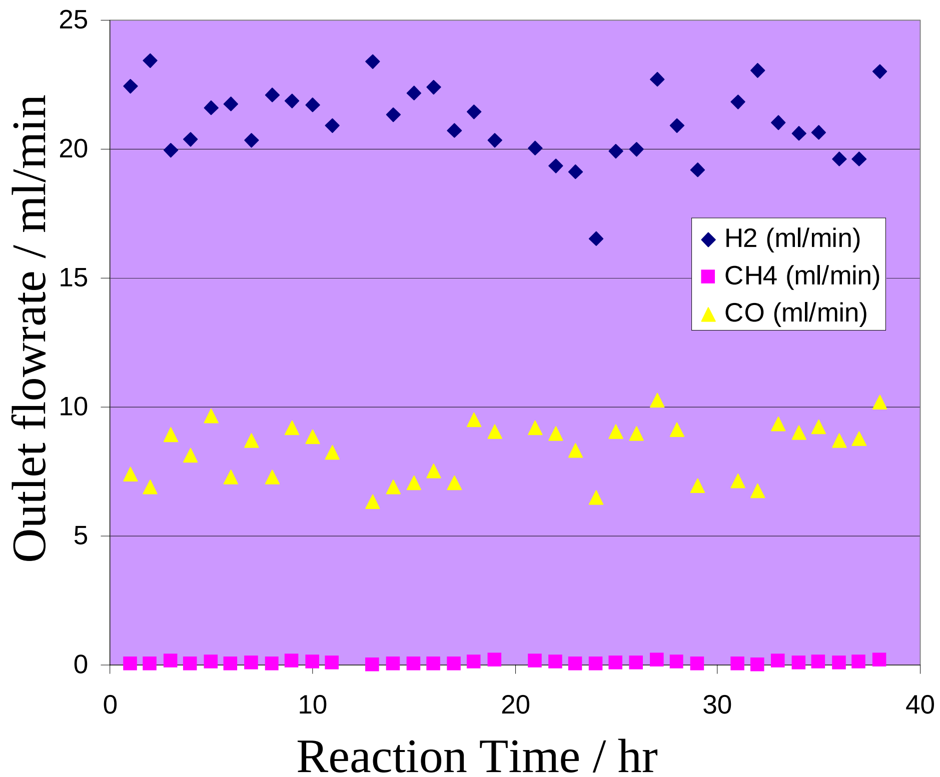
p-xylene



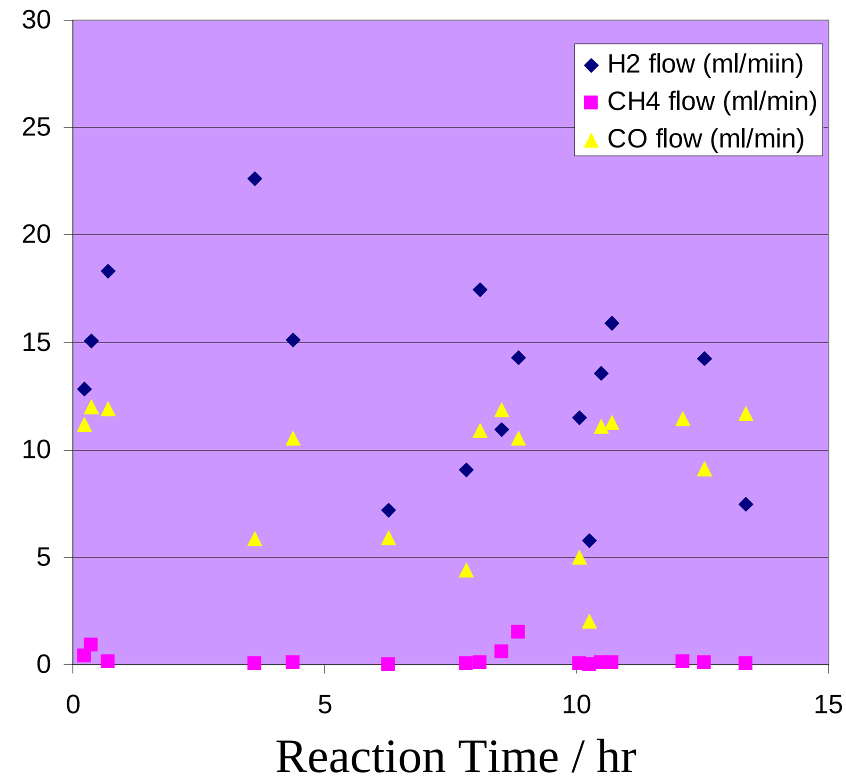
Los Alamos National Laboratory
Science Serving Society

Life time test over Ni/Al_2O_3
(750ºC, O/C = 0.76, H_2O/C = 1.15)

methane



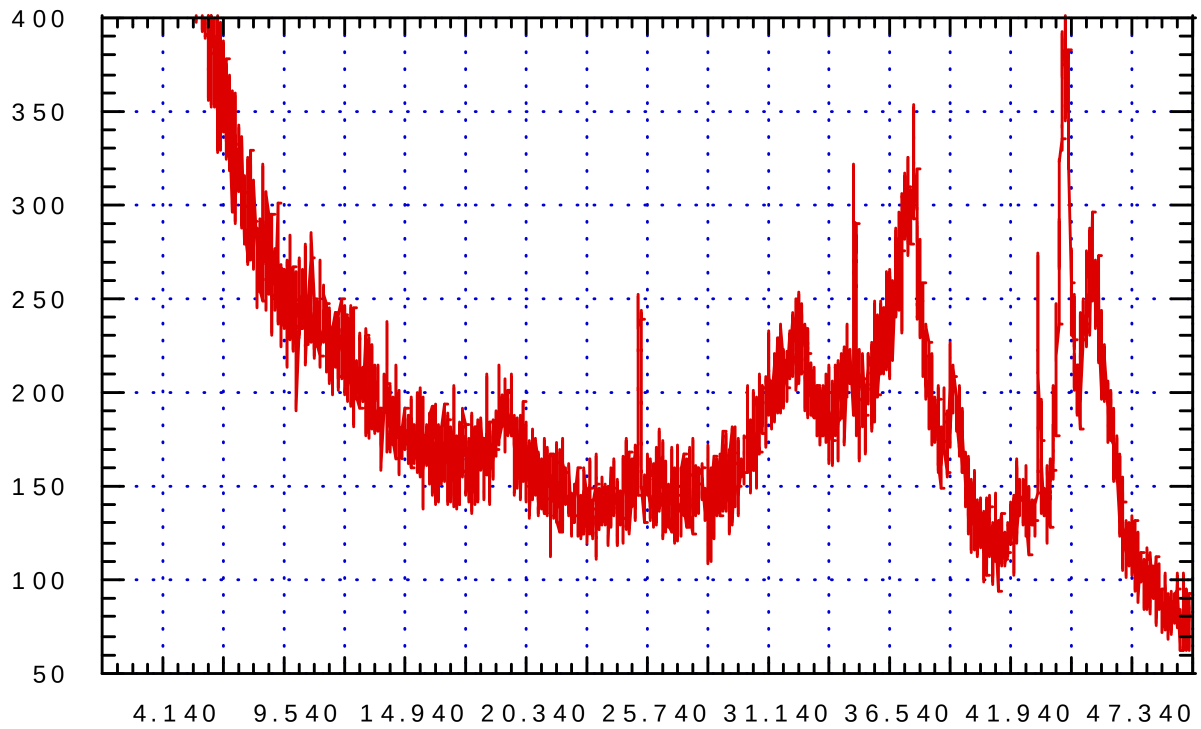
methyl cyclohexane



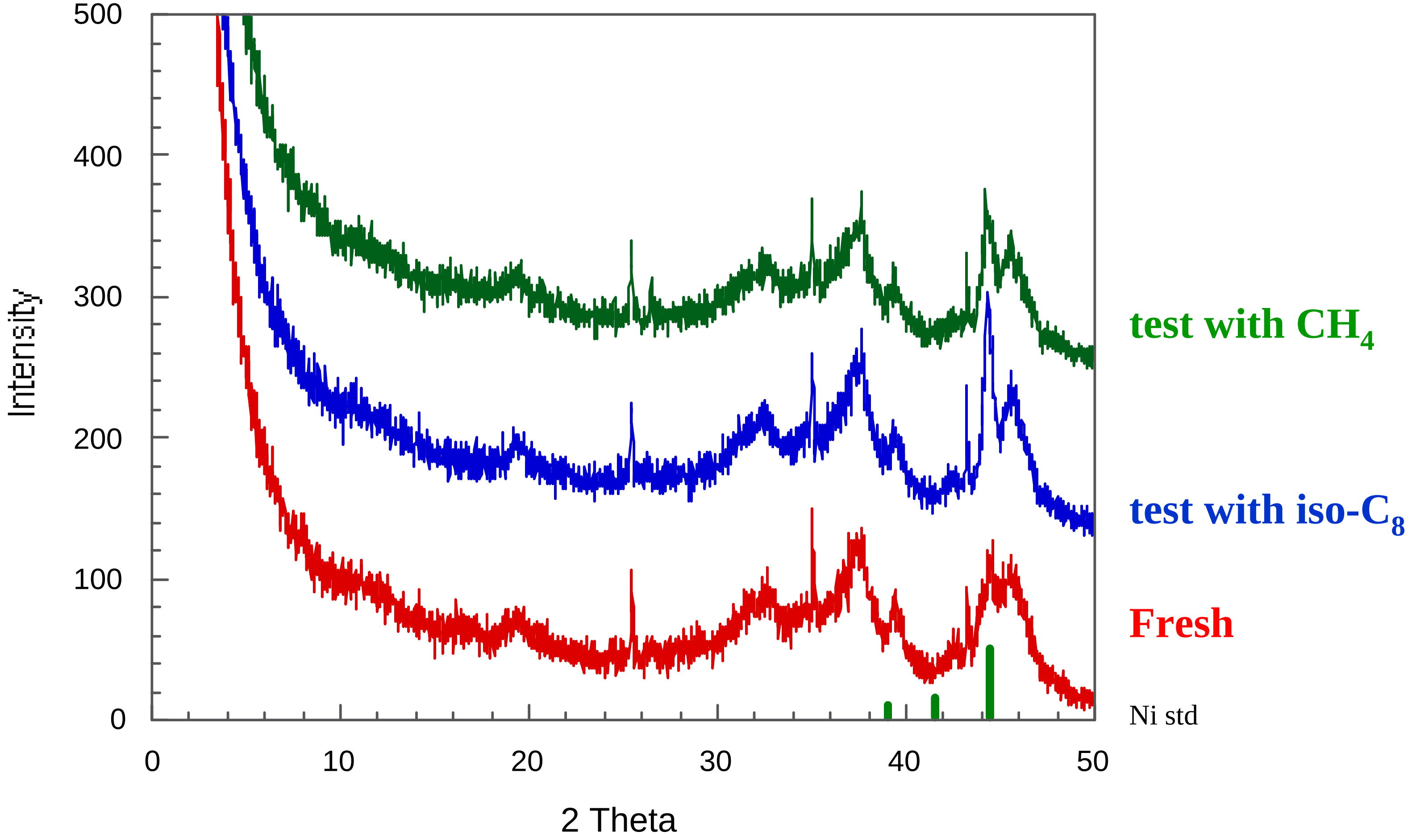
X-ray diffraction: 5% Ni/Al_2O_3

<u>Particle Size:</u>

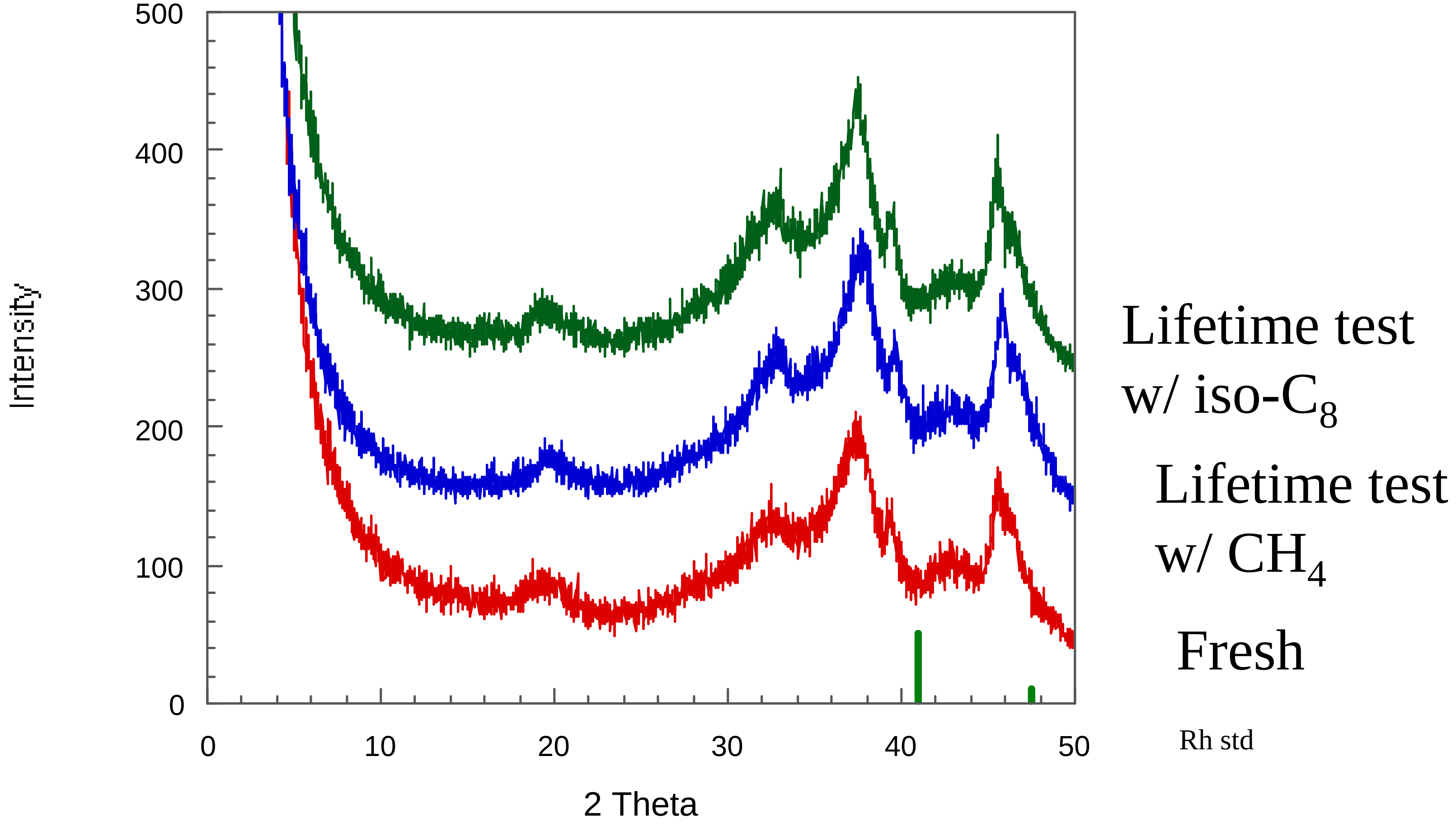
XRD	200 angstroms
Chemisorption	226 angstroms



X-ray diffraction: 5% Ni/Al_2O_3



X-ray diffraction: 0.5% Rh/Al_2O_3



CO Chemisorption Results

Sample# (Description)	**CO Chemisorption (cc_{STP}/g at 55 Torr)**	**Dispersion (%)**	**Crystallite Dia. (nm)**	**Metal Surface Area (m^2/g)**
1. (Fresh .5% Rh/Al_2O_3)	.4278	39.31	3.4	.718
2. (.5% Rh/Al_2O_3 with CH_4)	.1502	13.80	9.6	.254
3. (.5% Rh/Al_2O_3 with iso-octane)	Negligible	V. Low	V. Large	Negligible
4. (Fresh 5% Ni/Al_2O_3)	.970	5.08	24.1	1.40
5. (5% Ni/Al_2O_3 Lifetime test with iso-octane	.819	4.29	28.5	1.18
6. (5% Ni/Al_2O_3 Lifetime test with CH_4)	.164	.86	143	.235

All samples were heated under 400 Torr H_2 at 600°C for 1hr followed by $<10^{-6}$ vacuum at 600°C prior to measuring CO chemisorption.

XPS Post Characterization of Catalysts

Carbon 1s Spectrum for Ni/Al_2O_3 Catalysts

p-xylene

m-cyclohexane

pentene

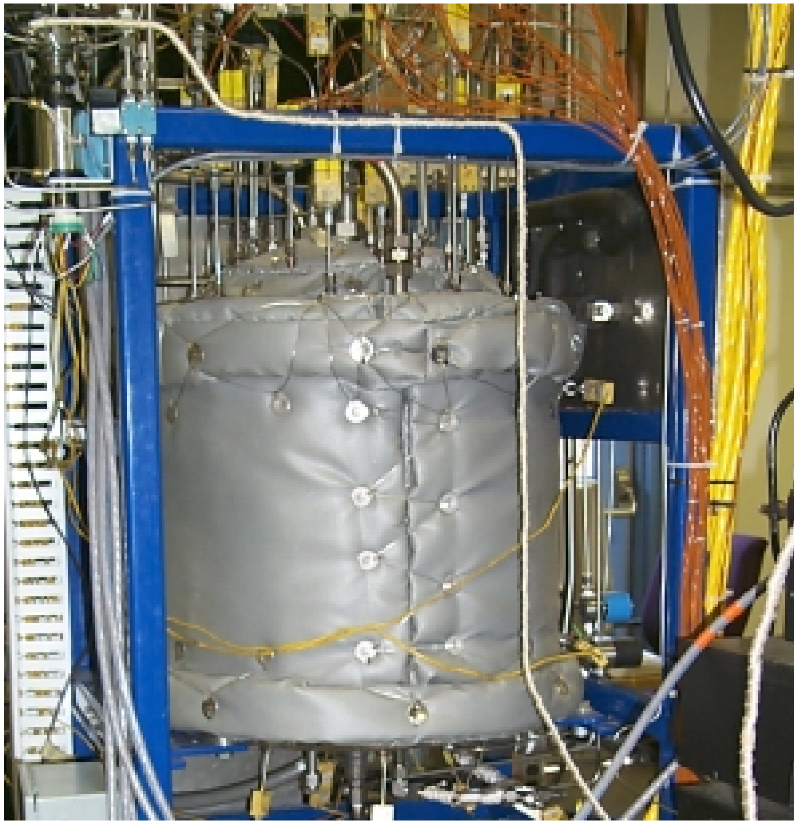
iso-octane

Binding Energy

- Elemental Analysis / Chemical Shift
  - large amounts of carbon formation:
    - p-xylene >> methylcyclohexane > 1-pentene >> iso-octane
  - NiC (nickel carbide) was formed with p-xylene
  - Carbon shifting to lower binding energies with increasing quantity
    - different carbon species?

HBT Reactor Test Facility

Integrated fuel processor for fuel testing

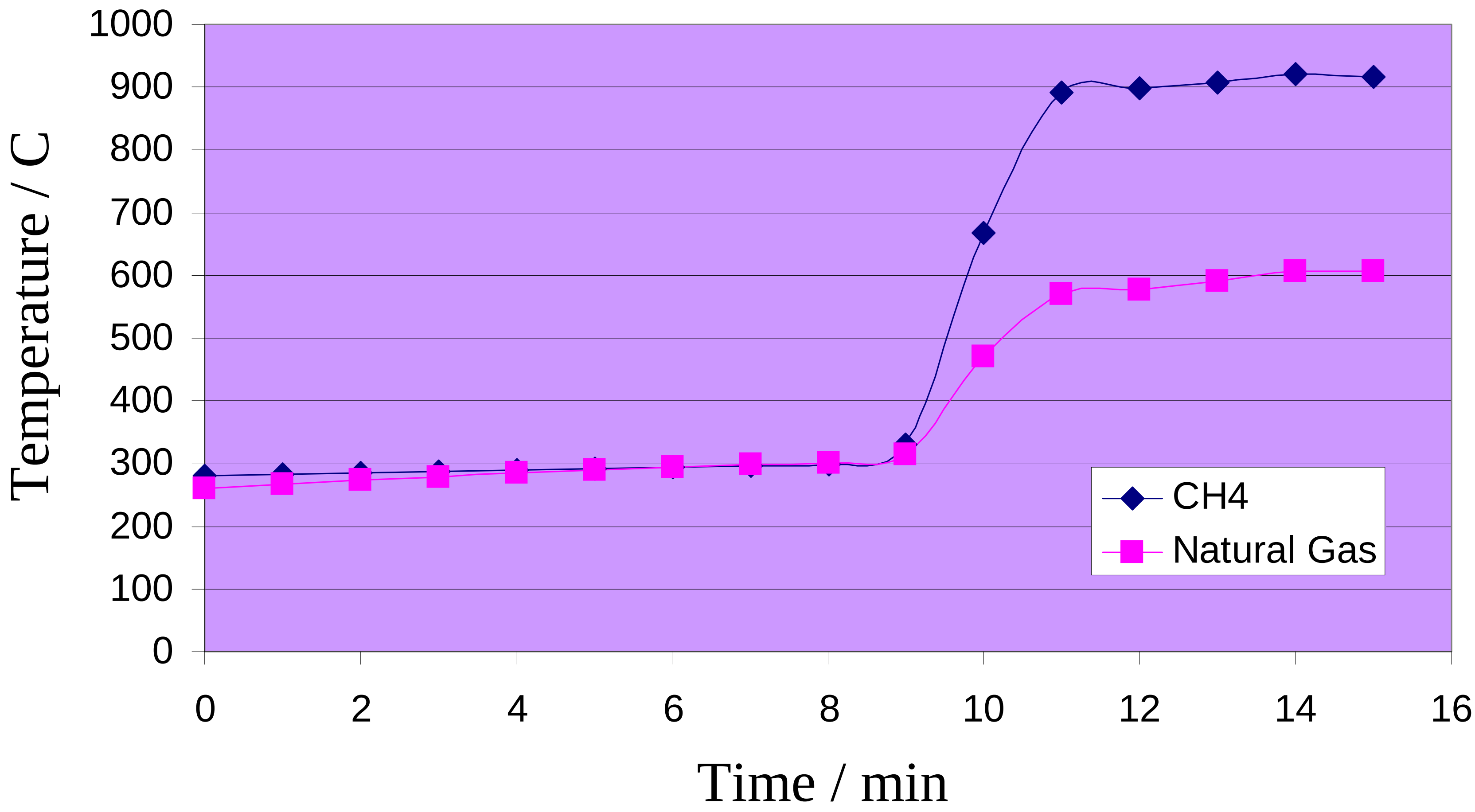


- Hydrogen Burner Technology

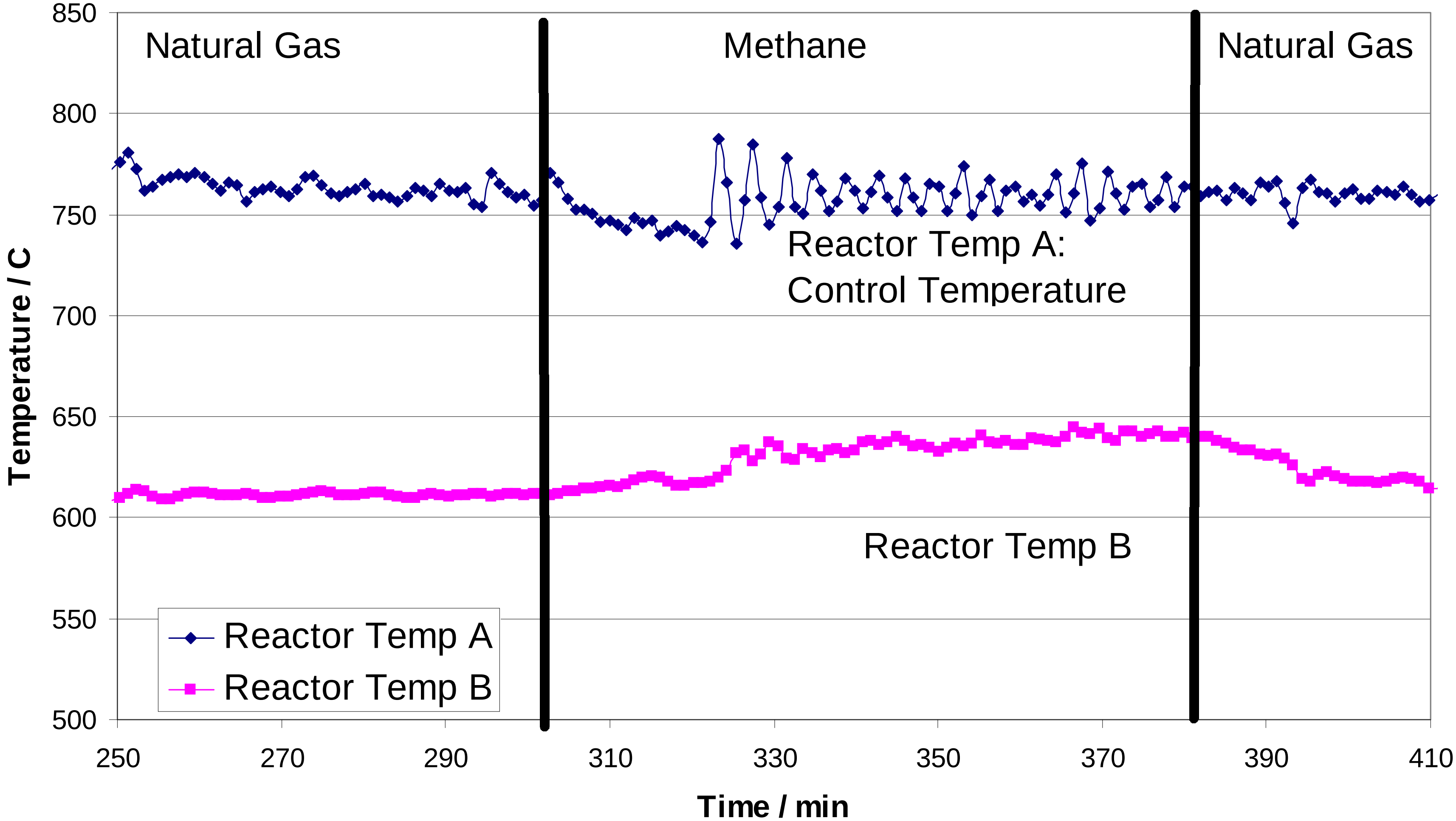
  Fuel-Flexible Fuel Processor (F3P)
  - Thermally-integrated fuel processor
  - Components: Partial oxidation reformer, high-temperature shift reactor, zinc-oxide sulfur removal bed, integral steam generator, combustion-driven fuel vaporizer
- Gas analysis equipment:
  - Gas Chromatograph (GC)
  - Mass Spectrometer
  - GC-MS
  - On-line HC, NO_x, O_2, CO, CO_2, CH_4

- Test Facility provides Balance-of-Plant framework for these fuel processors
  - Designed for accurate reactant management and emissions management for accurate heat and mass balances - efficiency measurement
  - Supervisory control hardware and software allow for transient operation and control

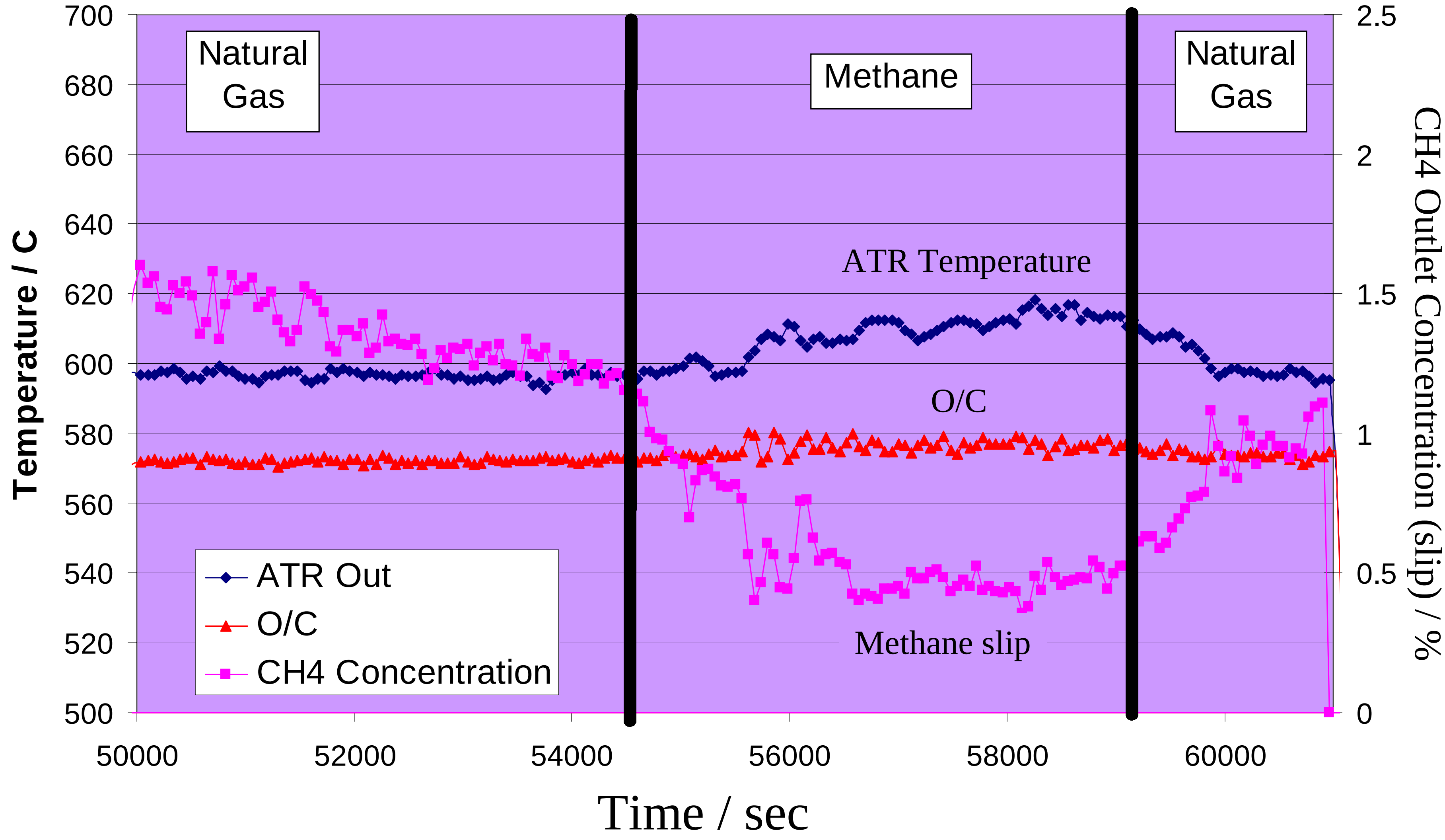
Fuel Processor Light-off:
Methane vs. Natural Gas



Fuel Composition Effects:
Natural Gas vs. Methane



Fuel Composition Effects:
Natural Gas vs. Methane



PNM Natural Gas Composition

Average Composition:

Ethane	1.4775%
Propane	0.203%
Butanes	0.06225%
Pentanes	0.0197%
C6	0.014375%
Methane	97.0675%
N_2	0.17175%
CO_2	0.9775%

Natural Gas /Methane Comparison

- Natural Gas
  - ΔH(Combustion:Stoich)

    213.95 kJ/mole (0.5%)

  - 100 molecule basis:
    - Flammable C: 101.1
    - Total C: 102.0
    - C-C Bonds: 2.24
  - POx ΔH(Comb:O/C=1)

    37.43 kJ/mole (5.0%)

- Methane
  - ΔH(Combustion:Stoich)

    212.8 kJ/mole

  - 100 molecule basis:
    - Flammable C: 100
    - Total C: 100
    - C-C Bonds: 0
  - POx ΔH(Comb:O/C=1)

    35.65 kJ/mole

Progress Summary

- **POX, SR, POX/SR of CH_4 and iso-Octane over Rh/Al_2O_3 and Ni/Al_2O_3**
  - **Monitoring inlet O_2/C ratio effect on conversion and selectivity**
  - **Monitoring effect of inlet H_2O on conversion and selectivity**
- **Preparation of in-house Ni/Al_2O_3 catalyst and test**
  - **commercial Rh, Ni**
- **Monitored sulfur effect on oxidation/reforming reaction**
- **HBT reactor operational**
  - **tested vapor fuels (natural gas / methane)**
  - **testing liquid fuels (CA reformulated, iso-octane, blends, …)**
- **Adiabatic POx/reformer operational**
- **Epyx reactor received**

Program Milestones:
Effects of Fuel Constituents on Fuel Processor Performance

Dec 99 Completed installation of HBT Fuel processing hardware including automation of the process control and safety hardware (Jan 00 upgraded to ATR)

Mar 00 Completed methane tests using the HBT fuel processor.

June 00 Complete initial testing of petroleum-based fuels.

Sept 00 Complete initial tests of EPYX hardware using natural gas and petroleum-based blends

May 00 Initial operation of partial oxidation reactor for fundamental measurements
Jul 00 Upgrade to include reforming/in situ carbon formation monitoring

Program Milestones:

Catalyst Designs for Improved Fuel Processing and Gas Clean-up within PEM Fuel Cell Engines

Dec 99 Complete automated testing instrument with fullflow programming, analytical measurements and data analysis

Mar 00 Complete first set of hydrogen generation experiments using test fuel on two or more catalyst types, through the temperature region of 400 to 1000 C

June 00 Complete series of short-residence-time experiments using test screens and foams

Sept 00 Complete series of experiments with micro-channel sections to achieve understanding of thermal effects on fuel processing reactions.

1999 Fuel Cell Review Comments

Fuel Composition Effect on Fuel Processing Dynamics: Nick Vanderborgh
On-Board Hydrogen Generation Technology: Jim Hedstrom

Comments:

Not clear that milligram-scale reactor will produce results that will be the same for a commercial reactor

Focus on testing fuels and on mechanistic catalyst characterization efforts

Focus on comparison of results between the micro reactor and a larger reactor

Address the issue of contaminants on the dynamic and durability of the fuel processor

Compare to successful commercial catalysts

Remember to address the issue of wall area-to-catalyst

Address long-term objectives

Reorganize this program into three teams (fuel processing, stacks and system)

Industrial Review Meeting (March 2000)

Comments: Concentrate on Understanding

LANL should work on items which increase the basic understanding of the area

The work should be basic but applied (basic to the general understanding of the work – applied so that the understanding can be used for industry development)

The work must provide the detail necessary so that the results can be used by industry for meaningful development.

Do not test commercial units which contain proprietary designs, catalysts, etc. but to test reactors which are documented, specifically to show gas and temperature profiles within the reactor, and also to evaluate the chemistry fundamentals of fuel processing (kinetics, carbon formation, catalyst degradation).

Industrial Review Meeting (March 2000)

Response: **Concentrate on Understanding**

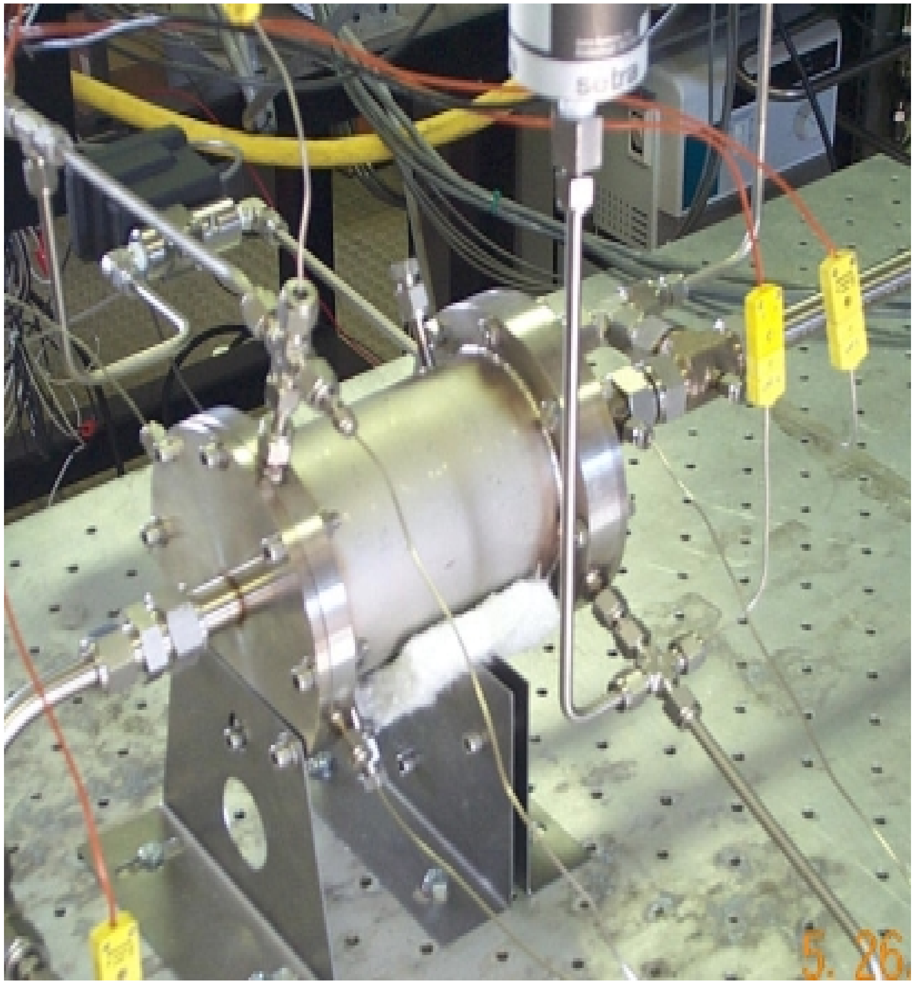
- **Developed 'non-proprietary' adiabatic partial oxidation reactor / steam reformer to test catalysts, measure reforming kinetics, measure *in situ* carbon formation in real-time**

- **Use exisiting iso-thermal POx/reforming reactor to evaluate catalysts, fuel formulations and catalyst durability**

- **Continue to use industrial reactor to test fuel formulations**
  - **Observe scale response**
  - **Heterogeneous vs. catalytic oxidation**

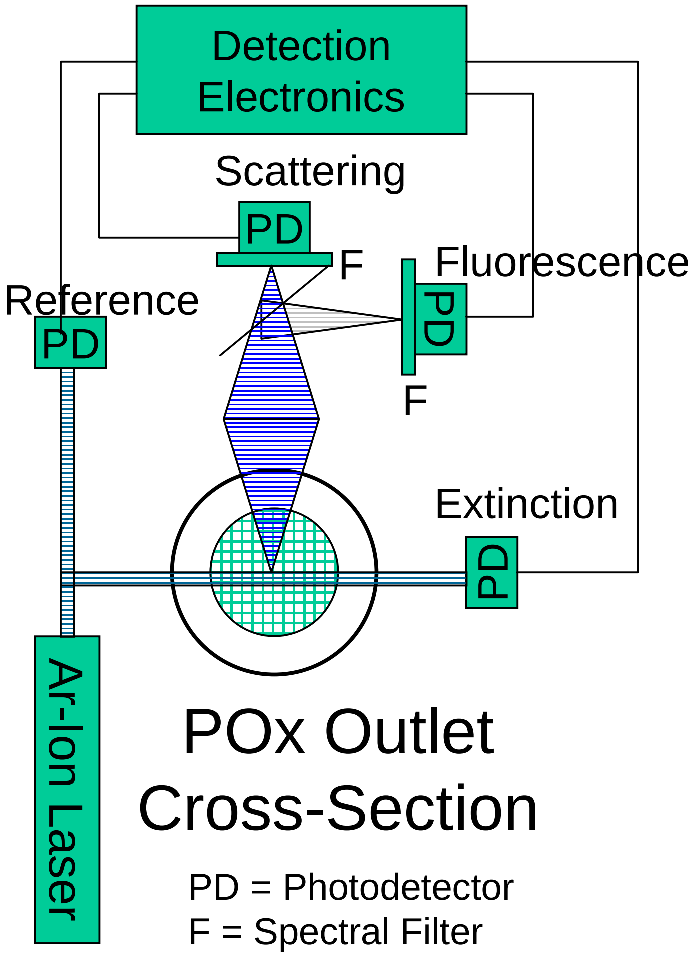
Adiabatic POx/Steam Reformer

Integrated fuel processor for fuel testing



- Partial oxidation
  - 3” O.D. x 1” monolith
  - supported noble metal (Pt)
  - gas composition & temperature profiles (radial)
- Steam reforming
  - Commercial nickel catalyst
  - packed bed and supported
  - gas composition & temperature profiles (axial and radial)
- Carbon Formation
  - laser for *in situ* monitoring of carbon formation

Measurement of Incipient Carbon Formation



POx Outlet Cross-Section

PD = Photodetector
F = Spectral Filter

- Simplified schematic of a laser scattering-extinction system (not all components shown)
- Laser scattering-extinction system provides a real-time measurement of carbon particles or soot formation
- Spectral Detection allows for fluorescence detection of PAHs – considered precursors to soot
- Flange with purged windows to allow optical access to outlet of POx
- Probe sampling coupled to online mass spec allows detection of higher AMU compounds (< 200 amu)

Interactions with industry

Hydrogen Burner Technology:

Testing integrated HBT reactor system

Provided ATR upgrade portion (Jan 00)

Epyx (Nuvera):

Received modular reactor (April 00)

Phillips:

Provide fuel for testing (naptha stream), fuel blends discussion about what the candidate fuels should be

Program Timing

Timing:

- **Project initiated in 1999 / Fuels testing initiated 2000**
  - **Part of Multi-year-program-plan Fuels for Fuel Cells (5 yr) program is still being developed**
- **HBT reactor operational with ATR Jan 00**
- **Adiabatic POx/reformer operational May 00**
  - **incorporate SR, in situ carbon formation monitoring Jul 00**
- **Epyx reactor received, operational Aug 00**
- **Direct comparison between micro Dec 00**
- **On set of carbon formation Mar 01**
  - **3 oxidation catalysts / 2 reforming catalysts**
  - **set of fuel blends (3) and components (4)**

Plans, future milestones

- **Examine fuel components, fuel blends, fuel impurity effects**

- **Adiabatic POx / steam reformer**
  - **Measure fuel composition effects on :**
    - ***in situ* carbon formation measured in real time**
    - **steam reforming kinetics**
- **Isothermal POx / steam reformer**
  - **lifetime tests with candidate fuels / catalysts**
    - **monitor catalytic activity with operation time depending on fuel constituents**
  - **evaluate the reforming kinetics as f(catalyst, fuel)**

- **Epyx (Nuvera) reactor operational**

- **Fuel effect comparison between catalytic and homogeneous partial oxidation**